

# EXHIBIT A



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## Invention Proposal

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John Hesch

Signed hard copy To: Xerox Intellectual Property Law Department HENRY FLEISCHER

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* If space for additional submitters is required, please use another sheet; and attach any supplementary Comments.				
Manager Paul Smith		Electronic Mail Address Paul.Smith2@crt.xerox.com	Bldg. No./MS XRCC/10	
Technical Category (see attached list) 4.2 Photoreceptors and Components		Name of Xerox Program (if any) none		
Opportunity for licensing revenue Who could be interested in it? How is this better than alternatives? Yes, customer unknown.				
Descriptive title of invention Preparation of Hyperbranched Polyarylethers by Direct One-Step Polymerization of Commercial Monomers.				
Describe the problem How was this problem tackled before your invention? The synthesis of hyperbranched polyarylethers described in the literature has been somewhat limited to polymerization of custom synthesized monomers. These monomers often take between 2 and 5 steps to synthesize. It would be of interest and importance to synthesize hyperbranched polyarylethers by direct polymerization of a mixture of commercially available monomers.				
Summary of the invention Describe briefly what the invention is and how it works in 5-8 lines. It is hypothesized that hyperbranched polyarylethers can be made by direct polymerization of a mixture of A <sub>2</sub> , B <sub>2</sub> , B <sub>3</sub> and B <sub>1</sub> monomers (where A <sub>2</sub> and B <sub>2</sub> are difunctional monomers, B <sub>3</sub> is trifunctional and B <sub>1</sub> is monofunctional). The branching units within the polymer are a result of the presence of the B <sub>3</sub> monomer and the tendency of polymerizations of this type to form crosslinked polymers is reduced or eliminated by the presence of a monofunctional B <sub>1</sub> monomer. The A <sub>2</sub> and B <sub>2</sub> monomers form the linear sections of the polymer. The known ability of polyarylethers to scramble themselves under typical polymerization conditions is an essential feature that makes this approach applicable to polyarylethers.				
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**Describe your invention** Describe how to make and use the invention and its novel embodiments. Cover the process, method, materials with sketches, flow charts, usage etc. What are the advantages of your invention for Xerox?

### Introduction.

Branched polymeric materials are not novel or new, they have been known for some time and are in common use. For example the difference between low-density polyethylene and high-density polyethylene is the amount of branching present within the polymeric structure. What is new, novel and of interest is the precise control of branching within a polymeric structure, and the introduction of that branching in a controlled and well defined manner. Perhaps the extreme example of such control of branching and polymeric structure is the synthesis of regular dendritic molecules. However, the application of such dendritic molecules is limited by the difficult multi-step procedures necessary for both their synthesis and purification (and the resulting high cost). The synthesis of hyperbranched materials is often a one step polymerization process (although their monomers often require multi-step synthesis) which is a simplification over the synthesis of truly dendritic structures. [General review: Kim, Y.H.; J. Polym. Sci. Pt. A, Polym. Chem., 2000, **38**, 1685-1698]

Hyperbranched materials have several advantages over linear materials of the same class. Branched materials (hyperbranches and dendrimers) will possess a lower solution and melt viscosities compared to their linear analogs owing to their lower hydrodynamic volume for the same molecular weight. Hyperbranched materials are often more soluble than their linear analogs, which is thought to be due to a decrease in the ability of the polymeric material to intertwine at a molecular level. Finally, hyperbranched materials can be thought to be a mid-point between linear polymers and crosslinked polymers since severing of or more of the branches will not result in a large loss of molecular weight.

A recent report by researchers at Dow Chemical describes a method for the synthesis of hyperbranched polycarbonates by a one step process. Reasonable to high molecular weights are obtainable using a four component system and careful control over both the addition order and addition rate. [Marks, M.J.; et al; J. Polym. Sci. Pt. A, Polym. Chem., 1996, **34**, 560-570.] Up to this report there has been only a few reports of hyperbranched polycarbonates.

Polyarylethers are another class of high performance polymers similar in structure to polycarbonates. Although there are numerous reports of hyperbranched polyarylethers they are typically made from multifunctional monomers that require custom synthesis. It would be of interest to synthesize and study hyperbranched polyarylethers made by one-step polymerization of a 4 component monomer system ( $B_3$ ,  $A_2$ ,  $B_2$  and  $B_1$ ). Polyarylethers are suited for such a synthetic approach due to their known ability to scramble their composition into an equilibrium composition under polymerization conditions. This occurs because a phenoxide will not only react at the polymer chain end but will react within the polymer chain resulting in a chain scission and recombination, with the formation of another reactive phenoxide (shown below in Figure 1 for the formation of an endgroup by reaction of a monofunctional monomer at either the chain end or at a mid-point within the chain).

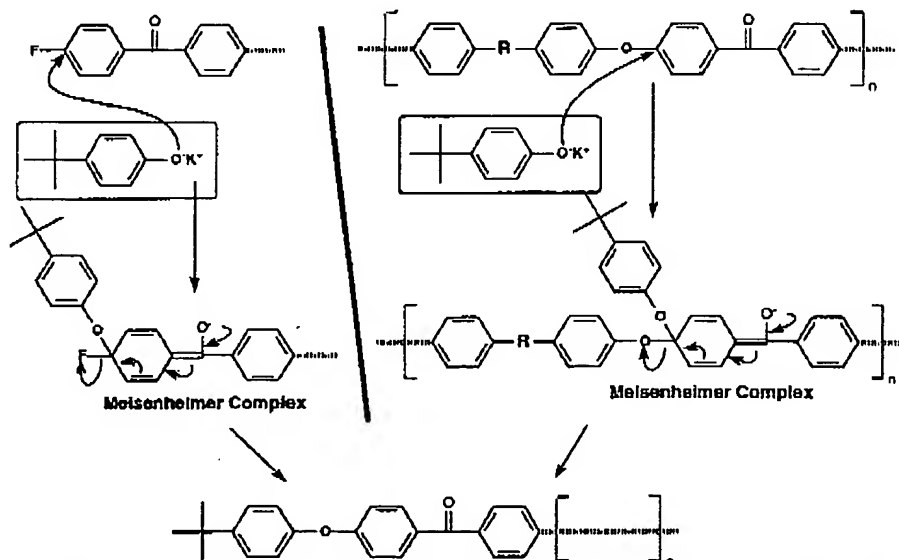


Figure 1. Reaction of a monofunctional monomer at either the polymer chain end (left) or mid-chain (right).

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**Concept.**

If one considers the four component system illustrated, copolymerization of THPE (branching unit), BPA and DFBP (linear unit) and tBP (chain terminator) will result in a polymeric system of the type shown. Variations in the ratio of monomers will result in the control over amount of branching and the length of the linear units.

**Model.****1. Lengthening of the linear portion of the polymer only.**

A computer model has been constructed to illustrate this concept. If one considers only lengthening the linear portion ( $n$ ) of the branched molecule (see Figure 2 below) then for each increasing generation ( $n$ ) the changes in relative monomer concentrations are most dramatic at lower generations (low molecular weight) and become negligible at higher molecular weight (see Figure 3). This implies that the changes in physical properties of the resulting branched molecules are smallest when the linear portion of the molecule is predominant and largest when the length of the linear portion (generation,  $n$ ) is between 1 and 10. Using this method the molecular weight of the final branched polymer is controlled by the ratio of  $B_3/B_1$  monomers to  $B_2$  monomer present in the polymerization.

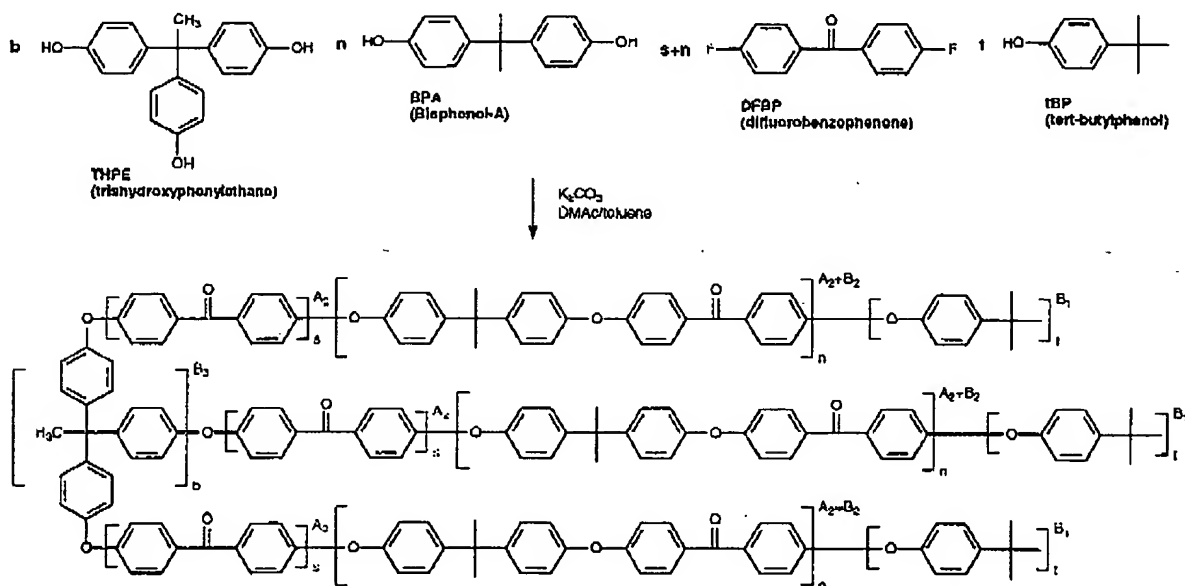


Figure 2. Hyperbranched polyarylethers by direct polymerization of four monomers. Model 1, variation in linear portion of branched polymer with control over final polymer molecular weight.

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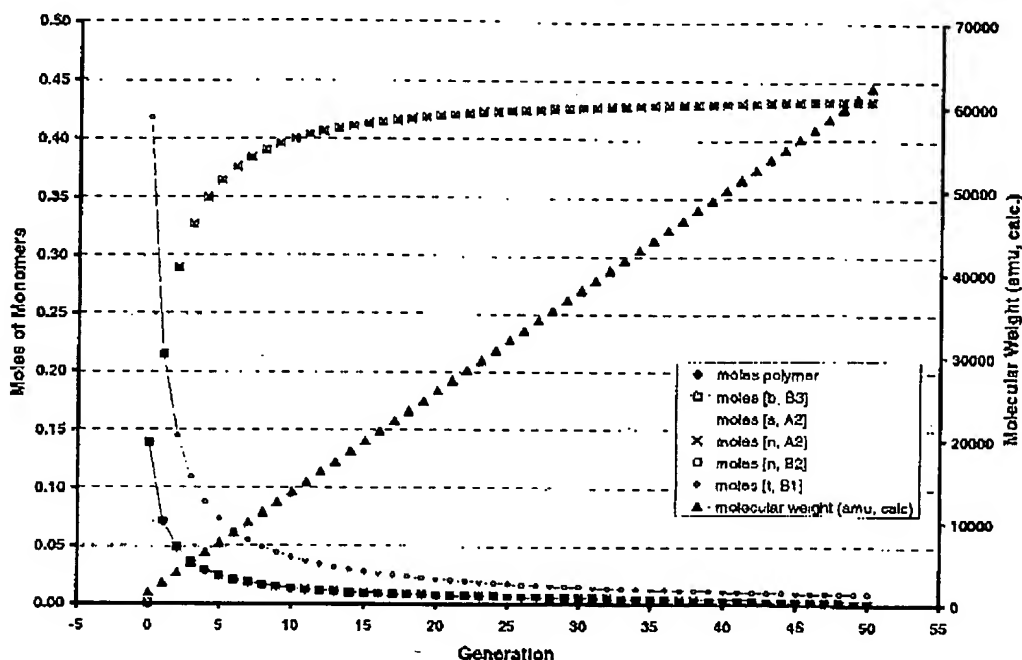


Figure 3. For branched polymers of type illustrated in Figure 2; Calculated relative molar concentrations of each of 4 monomers for the type of branched molecule illustrated, as a function of generation (n, linear chain length).



Microsoft Excel  
Worksheet

Additional Information:

masses of each needed to carry out polymerization.

Electronic version of the model worksheet illustrating relative molar concentrations of monomers and

## 2. Variation of the branched unit to linear unit ratio (by variations in ratio of $B_3$ and $B_2$ monomers).

Variations in the relative amounts of  $B_3$  and  $B_2$  monomers used in this 4 component system provides a method by which the amount of branching within the polymer can be controlled. Again a monofunctional  $B_1$  monomer is used to control/eliminate the ability of this system to crosslink. In this case for every branching unit present in the polymer 2 molar equivalents of difunctional  $A_2$  monomer and 1 molar equivalent of monofunctional  $B_1$  monomer is necessary to balance the stoichiometry and hence there is no inherent control over molecular weight. The system will reach its equilibrium molecular weight for its given experimental conditions (concentration, temperature, base used etc.) Figure 4 below illustrates the idealized branched polymer, however in real practice the placement of branching units and length of branching units would be randomly distributed throughout the polymer structure.

A computer model has been constructed (Figure 5) in order to illustrate changes in repeat unit molecular weight and molar amounts of each component as a function of mole fraction of  $B_3$  monomer (relative to  $B_2$  monomer).

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Invention Proposed (Office 97)



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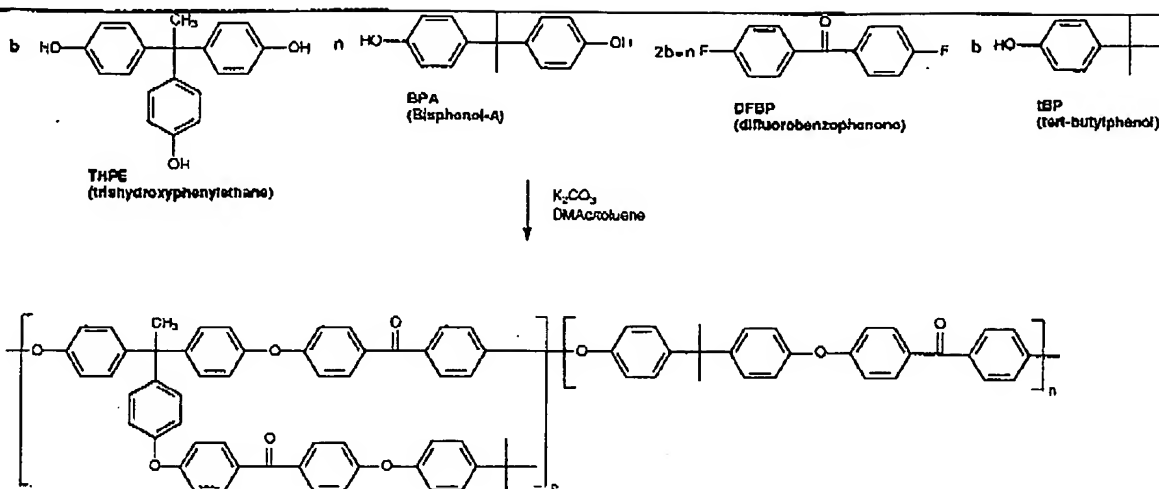


Figure 4. Hyperbranched polyarylethers by direct polymerization of four monomers. Model 2, variation in ratio between  $B_3$  and  $B_1$  monomer (control over amounts of branching present in molecule).

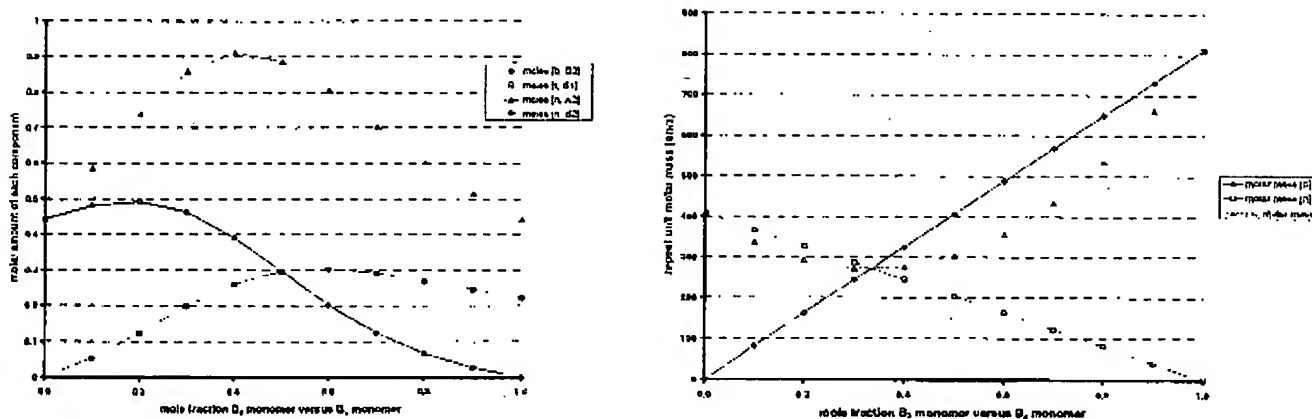


Figure 5. For branched polymers of type illustrated in Figure 4; calculated molar amounts (left) and repeat unit molar mass (right) for mole fractions of  $B_3$  monomer from 0.0 to 1.0.



Microsoft Excel  
Worksheet

Additional Information: Electronic version of the model worksheet illustrating relative molar concentrations of monomers and masses of each needed to carry out polymerization.

### Reduction to Practice.

Not reduced to practice, work is in progress.

### Application of hyperbranched materials.

Materials of this sort may have application as binder materials for dual-layer and single-layer photoreceptors. Their branched nature may impart

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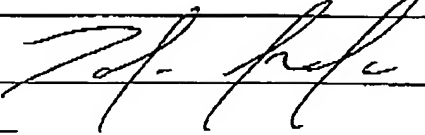
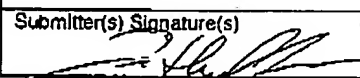


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improved wear resistance to OPCs under BCR charging conditions.

**Embodiments.**

1. Hyperbranched polyarylethers and their method of synthesis/preparation as outlined.

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